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Photo-RDRP for everyone: Smartphone light-induced oxygen-tolerant reversible deactivation radical polymerization☆

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A B S T R A C T

Oxygen-tolerant reversible deactivation radical polymerization (RDRP) was carried out utilizing a smartphone flashlight. Well-controlled poly(oligo(ethylene oxide) monomethyl ether methacrylate) ($POEOMA_{500}$) with relatively low dispersity ($Đ = 1.16–1.35$) was obtained employing dual catalysis atom transfer radical polymerization (ATRP) with $CuBr_2$/tris(2-pyridylmethyl)amine (TPMA) and three different organic photocatalytic dyes (i.e. eosin Y (EY), fluorescein (FL), and riboflavin (RF)). The smartphone flashlight was also used for carrying out oxygen-tolerant photoinduced electron/energy transfer (PET) reversible addition–fragmentation chain transfer (RAFT) polymerization with EY and dithioesters RAFT agents , and photoiniferter (PI) RAFT polymerization with trithiocarbonate RAFT agent. The formation of crosslinked gels and facile measurement of gel points via recording the gelation process by in-built smartphone camera was also demonstrated.

1. Introduction

Reversible deactivation radical polymerization (RDRP), also known as controlled radical polymerization (CRP), is a powerful technique for synthesizing well-defined functional polymers. This technique presents several fascinating merits, including the formation of low dispersity (co) polymers with wide architectural diversity, high chain-end fidelity, and applicability to various monomers, solvents, and tolerance to impurities [1–3]. These advantages have propelled RDRP advances into many areas such as drug delivery, coatings, electronics, and agriculture [4–8]. The most widely used methods are atom transfer radical polymerization (ATRP), reversible addition-fragmentation polymerization (RAFT), and nitroxide-mediated radical polymerization (NMP) [2,9–11]. The versatility of RDRP has realized controlled radical polymerization of different monomers using various unconventional but yet interesting catalysts (i.e. red blood cells, 1 penny copper coins and bacteria) [12–15] and media (i.e. whisky, beers, honey and rain water) [16–19].

ATRP is a reversible redox process, that typically employs transition metal complexes (i.e., copper, ruthenium, or iron) to intermittently activate alkyl halide and generate radicals that react with vinyl monomers [20,21]. On the other hand, RAFT polymerization relies on a degenerative transfer mechanism through dynamic exchange of thiocarbonylthio compounds (coined chain transfer agents, CTA) with radicals [22,23]. For ATRP, it is crucial to maintain a dynamic equilibrium between prevalent dormant species and minute amounts of active radicals. Intermittent activation provides concurrent growth of all chains, and low radical concentration diminishes radical termination.

Smartphones are interwoven into all aspects of our life with approximately 7 billion current users [24]. Smartphones are equipped with numerous applications, sensors, cameras, and flashlights (typically white LED or Xenon light) that have made them ubiquitous in many daily activities. Their flashlights present a relatively uniform light wavelength and intensity within the same model, which explains the current growing interest in their use for a plethora of applications from 3D-printing [25,26], analyte detection [27], spectroscopy [28], and biosensing [24]; however, the use of smartphones as a tool for photochemical synthesis has remained unexplored.

The advances in photochemistry have revolutionized RDRP and have generated new pathways for temporal and spatial control for RDRP [29–32]. Thus, RDRP has transformed from a very arduous process that required stringent deoxygenation (i.e., freeze–pump–thaw, nitrogen sparging, or using glove box) and long reaction times to simple, rapid, and energy-efficient experimental procedures with a tolerance to oxygen [33–37]. Nevertheless, limited accessibility to uniform and standardized light sources and inconsistency of different photoreactors (i.e. light intensity, the distance between source and reactor, reactor geometry, and temperature control) resulted in batch-to-batch variations and limited reproducibility of photochemical reactions [38–40]. While some commercial photoreactors (e.g., Kessil or EvoluChem) have attempted to surmount the problems of custom-made photoreactors, their price, and availability, especially in the resource-limited areas, have been a great constraint to their more general adaptability. With the growing interest

☆ This contribution is dedicated to Professor Nikos Hadjichristidis on the occasion of his 80th birthday.

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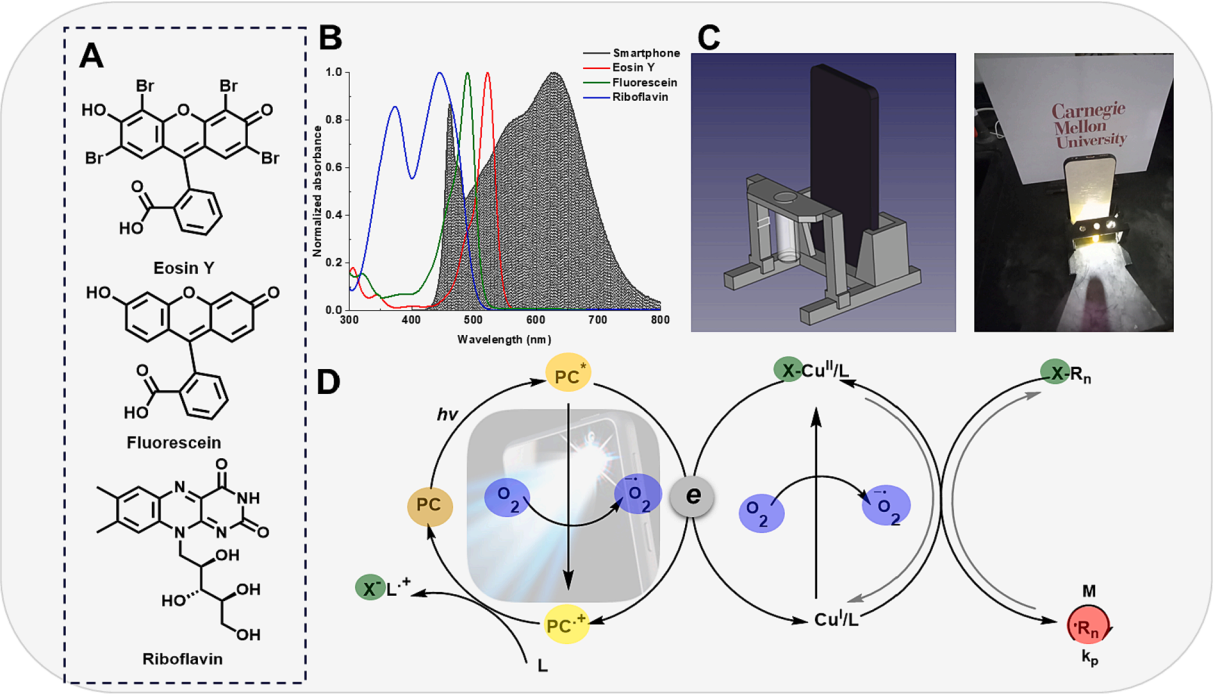


Fig. 1. (A) Chemical structures of EY, FL, and RF. (B) UV–VIS spectra of EY, FL, and RF compared to the emission of smartphone light. (C) Schematic and photograph of the experimental set-up for smartphone-induced RDRP. (D) Mechanism of dual catalysis ATRP in the presence of Cu/ligand (L) and PC.

Table 1
Properties of polymers synthesized by smartphone ATRP of $OEOMA_{500}$ in the presence of different photocatalysts and smartphones.[(a)]

Entry	PC	Light	Time (h)	[b]Conv(%)	$M_{n,the}$ x1,000	[c]$M_{n,abs}$ x1,000	[c]$Đ$
1	EY	iPhone 6	6	85	85.2	96.2	1.23
2[d]	EY	iPhone 6	7	95	95.2	87.3	1.22
3[e]	EY	iPhone 6	6	31	31.2	42.2	1.16
4	FL	iPhone 6	17	93	93.2	91.8	1.30
5	RF	iPhone 6	6	95	95.2	99.8	1.35
6[f]	EY	iPhone 6	6	97	97.2	246.7	2.65
7	EY	iPhone 5	6	90	90.2	113.1	1.25
8	EY	A31	6	>99	100.2	120.3	1.26

(a) Reactions conditions: $[OEOMA_{500}]_0/[HOBiB]_0/[CuBr_2]_0/[TPMA]_0/[PC]_0$ = 200/1/0.2/0.6/0.04, irradiated with Iphone 6 in 1.5 mL dram vial unless otherwise stated. $[OEOMA_{500}]$ = 300 mM, in aqueous PBS with DMSO (10 % v/v). (b) Monomer conversion was determined by using ^{1}H NMR spectroscopy. (c) Molar mass ($M_{n,\ abs}$) and dispersity ($Đ$) were determined by GPC analysis (DMF as eluent). Absolute molar mass ($M_{n,abs}$) was determined using dn/dc values of $POEOMA_{500}$ = 0.05; dispersity ($Đ$) values were recorded from refractive index traces. (d) Polymerization was carried out in an open-to-air glass vial. (e) DMSO was used as a solvent. (f) Without $CuBr_2$.

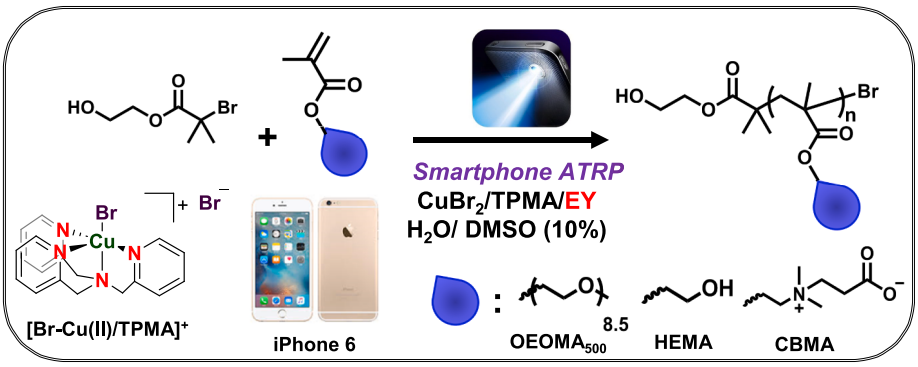
in carrying out RDRP outside of lab settings in applications spanning from 3D-printing [41,42], surface initiated (SI) polymerization [43–46], signal amplification [47,48], and microfluidics [49–51], the need for a uniform, portable and reliable photoreactor is also enhancing.

We recently reported the photo-ATRP of methacrylates/acrylates using a dual catalytic ATRP system employing $CuBr_2$/tris(2-pyridylmethyl)amine) (TPMA) and eosin Y (EY) as photocatalyst (PC) in aqueous environment [52–54]. Well-defined polymers were formed in a short reaction time (30 min) in open-to-air vials after irradiation with green light (λ_{max} = 520 nm) using LED lamps. This prompted us to further investigate a more general and universal system for the polymerization of oligo(ethylene oxide) monomethyl ether methacrylate ($OEOMA_{500}$) using irradiation generated from smartphones flashlight by leveraging three distinct dyes: EY, fluorescein (FL), and riboflavin (RF) (Fig. 1A). While the efficiency of EY for dual catalytic ATRP with green light (λ_{max} = 520 nm) was previously disclosed, the use of FL and RF for dual catalytic ATRP has never been studied before [55]. As depicted in Fig. 1B, the absorption of all three PC overlaps with the emission of white light generated from smartphones, suggesting that all dyes should take part in photochemical reactions. Tested smartphones (Table 1) produced consistent light with adequate intensity (9.3 mW/cm^2 at λ = 450 nm) over time. The measured intensity depends on the distance to the reactor (Figure S1-S3).

2. Results and discussion

Oxygen tolerant ATRP. The first experiments were performed with iPhone 6 (Apple), EY as a photocatalytic dye, $CuBr_2$/TPMA complex, and 2-hydroxyethyl α-bromoisobutyrate (HOBiB) as an initiator, in phosphate buffer saline (PBS) water and DMSO (10 % v/v) (Scheme 1). The vial was placed at a 2.5 cm distance from the smartphone flashlight source in a completely dark room (Fig. 1C). Importantly, due to the tolerance of dual catalytic ATRP to oxygen, the polymerization was performed without any deoxygenation in a closed cap vial (without stirring) [53,56].

After 6 h of irradiation with a smartphone flashlight, the monomer conversion was 85 %, and polymers with low dispersity ($Đ$ = 1.23) were obtained (entry 1, Table 1, Figure S4 for SEC traces). To further demonstrate the oxygen tolerance of the system, polymerization was also carried out in an open-to-air glass vial (entry 2, Table 1). In this case, the polymerization still proceeded with good control ($Đ$ = 1.22), but the polymerization was slower (7 h). The remarkable oxygen tolerance of dual catalytic ATRP can be attributed to the reduction of O_2 to $O_2^{\bullet-}$ (superoxide anion) via single electron transfer (SET) from excited states of the photocatalyst (PC*), or conversion of triplet to singlet oxygen which can further react with DMSO to form dimethyl sulfone ($DMSO_2$) [57,58]. Additionally, the continuous generation of Cu(I) via oxidative/reductive quenching of PC can act as a contributor to the oxygen scavenging in the system (Fig. 1D). Furthermore, polymerization of $OEOMA_{500}$ was demonstrated in an organic solvent (i.e., DMSO) with very good control ($Đ$ = 1.16, entry 3, Table 1).



Scheme 1. General scheme for the polymerization of $OEOMA_{500}$, HEMA or CBMA via dual catalysis ATRP with $CuBr_2$/TPMA and EY via irradiation with a smartphone flashlight.

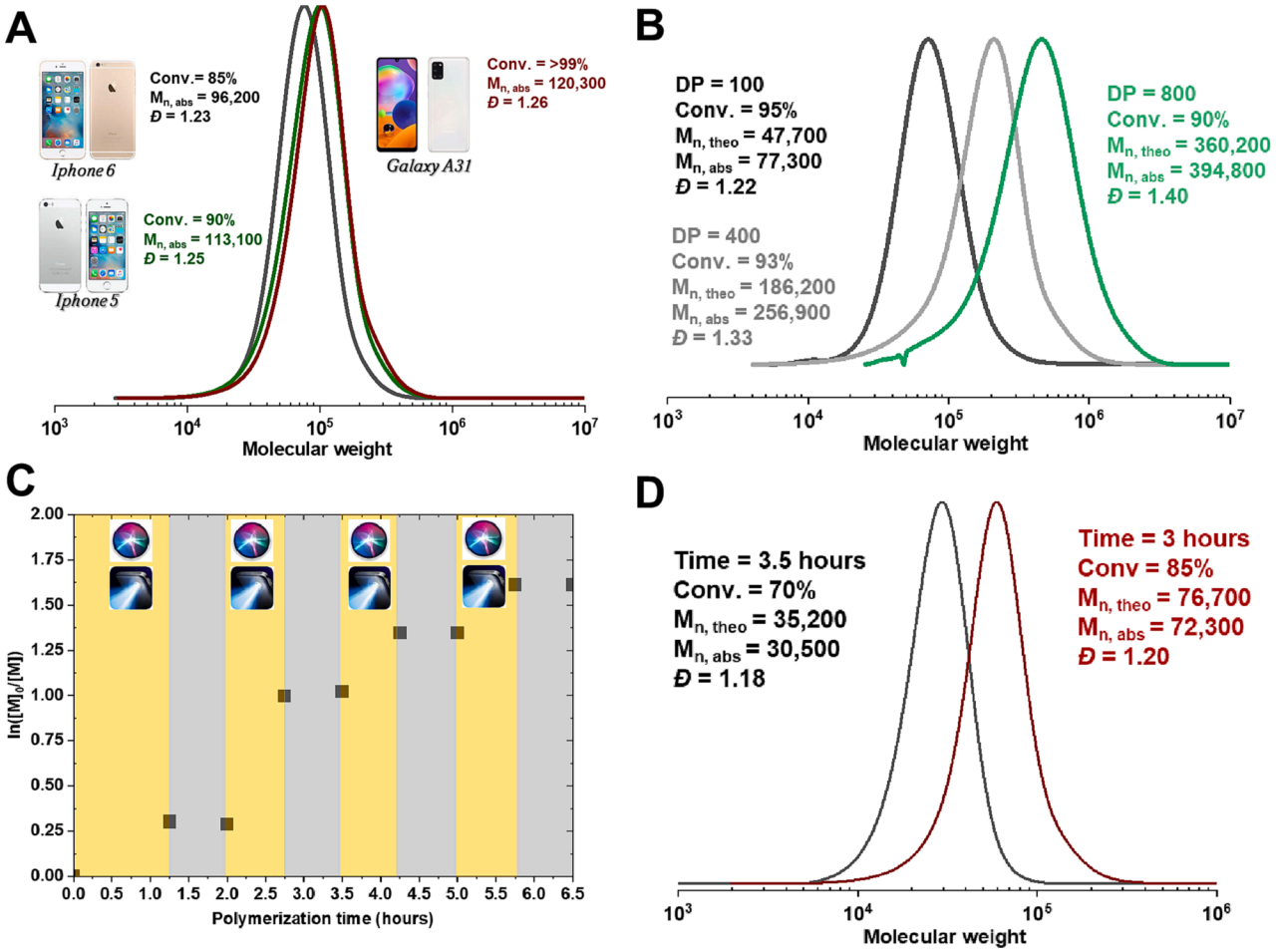
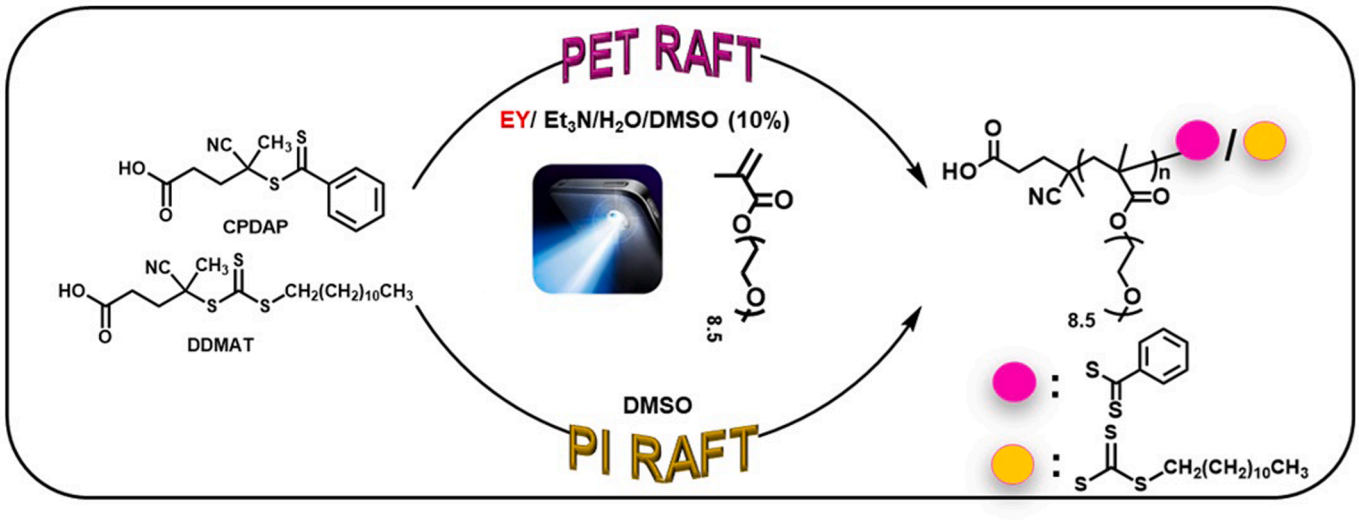


Fig. 2. The results for ATRP of $OEOMA_{500}$ with $CuBr_2$/TPMA and EY. (A) SEC traces in the presence of different smartphone flashlight irradiation. (B) SEC traces of $POEOMA_{500}$ synthesized at different target DPs. (C) Temporal control of polymerization. (D) SEC traces of chain extension experiments of $POEOMA_{500}$.

The polymerization with FL afforded polymers with $M_{n,abs} = 91,800$ and $Đ = 1.30$, but at a much longer time (17 h, entry 4, Table 1). This could be attributed to the higher fluorescence quantum yield ($\Phi = 0.95$) of FL than EY ($\Phi = 0.57$), despite the fact that FL is a stronger reducing agent at excited state ($E^{*red}(PC^{+\bullet}/PC^{*}) = -1.22$ for FL and -1.1 for EY vs. SCE) [59]. The polymerization using RF as a PC afforded polymers in the same period as EY (6 h) although the polymers had higher dispersity ($M_{n,\ abs} = 99,800$, $Đ = 1.35$, entry 5, Table 1).

The control experiments revealed no conversion in the absence of EY or ambient light after 6 h. In addition, polymerization under metal-free ATRP conditions (without $CuBr_2$) [60,61] resulted in very poor control of polymerization ($M_{n,abs} = 246,700$, $Đ = 2.65$, entry 6, Table 1). Finally, polymerization using other smartphones such as iPhone 5 (Apple, 9.7 mW/cm^2 at $\lambda = 450$ nm) and Galaxy A31 (Samsung, 14.1 mW/cm^2 at $\lambda = 450$ nm) yielded polymers with high conversion (90 % and > 99 %, respectively) and low dispersity ($Đ = 1.25$ and 1.26, respectively). Galaxy A31 yielded a faster polymerization, due to higher flashlight intensity (Figure S1).

The molecular weight distributions for polymers prepared using all three smartphones were symmetrical and monomodal (Fig. 2A). The



Scheme 2. Polymerization scheme to synthesize $POEOMA_{500}$ via PET RAFT and PI RAFT polymerization.

polymerization followed first-order kinetics indicating a constant concentration of propagating radicals throughout the reaction (Figure S5). Approximately 1 h induction period was observed, depending on the container size.

Versatility of ATRP. To further demonstrate the versatility of smartphone-induced ATRP, the polymerization of $OEOMA_{500}$ with different target degree of polymerization (DP) were tested. Polymers with molecular weights from 77,300 to 394,800 were generated using EY as a PC (Fig. 2B). The molecular weight distribution of the polymers remained monomodal for all targeted DPs (100, 400, and 800) with relatively low dispersity ($Đ$ = 1.22, 1.33, and 1.40, respectively). Initiation efficiencies (I*) were limited, especially at lower DP (I* = 62 %, 74 %, and 91 %, respectively). This could be due to termination of some initiating radicals by O_2 as previously reported in oxygen tolerant systems [52,62,63]. Polymerizations of other hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA) and zwitterionic monomer, 3-[[2(methacryloyloxy)ethyl]dimethyl-ammonio]propionate (CBMA), were successfully carried out, yielding well-controlled polymers with relatively low dispersity ($Đ$ = 1.21 and 1.41) (Figure S6).

An important feature of smartphone flashlights is the ability to switch on/off light with only verbal commands by the virtual assistant (SIRI for iPhone). Therefore, the temporal control of dual catalytic ATRP was studied via communication using SIRI. This is an important feature given the current interest in automation and external control for RDRP [64–67]. Interestingly, the polymerization in the presence of smartphone light progressed without any operator's physical interaction and immediately stopped when the light source was turned off with verbal commands such as "SIRI, turn on/off the flashlight" (Figure S7). This cycle was repeated several times with complete resumption and cessation of polymerization each time (Fig. 2C). The polymers obtained from this on/off cycle were monomodal with a low dispersity ($Đ$ = 1.24) (Figure S8). In the next part of the study, the chain end fidelity of polymers produced by smartphone light was evaluated via a chain extension experiment. The $POEOMA_{500}$ ($M_{n,\,abs}$ = 30,500 and $Đ$ = 1.18) was isolated and used as a macroinitiator for chain extension. Adding a new portion of $OEOMA_{500}$ (target DP = 100) followed by irradiation with a smartphone afforded the second block of $POEOMA_{500}$ ($M_{n,abs}$ = 72,300 and $Đ$ = 1.20). The SEC trace in Fig. 2D shows that the chain extension of $POEOMA_{500}$ was successful without any unreacted macroinitiator remaining.

Oxygen tolerant RAFT polymerization. Given the success in ATRP of methacrylates induced by smartphone flashlights, we extended it to other RDRP methods. First, we investigated photoinduced electron/energy transfer reversible addition–fragmentation chain transfer (PET-RAFT) polymerization. PET-RAFT employs visible light to excite photo redox catalysts (e.g. zinc tetraphenylporphyrin, tris[2-phenylpyridinato-C2,N]iridium(III), eosin Y, or semiconductors) to activate RAFT agents via SET [39,68–73]. For aqueous PET-RAFT, 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPDAP) was used as CTA, $OEOMA_{500}$ as a monomer, EY as photocatalyst, and triethylamine (Et_3N) as an electron donor in a closed cap vial but without deoxygenation (Scheme 2, Figure S9 for SEC traces). The first experiment using $[OEOMA_{500}]_0$ = 300 mM and target DP = 200 yielded polymers after a long reaction time (15.5 h) with high dispersity ($Đ$ = 1.58; entry 1, Table 2). However, at lower target DP (DP = 100) and higher monomer concentration ($[OEOMA_{500}]_0$ = 800 mM), notable improvement in polymerization time (6 h, Conv. = 54 %) and polymers dispersity ($Đ$ = 1.24) was observed (entry 2, Table 2).

The smartphone was also employed for photoiniferter (PI) RAFT polymerization, which relies on the absorption of visible light via forbidden n–π* transition in trithiocarbonates RAFT agents, and subsequent radical generation via homolytic cleavage [74]. The moderate oxygen tolerance of photoiniferter RAFT polymerization was reported in the literature and attributed to oxidation of the thiocarbonylthio compound and O_2 reaction with radicals generated from RAFT agent

Table 2
Properties of polymers synthesized by PET-RAFT polymerization and PI RAFT polymerization of $OEOMA_{500}$ in the presence of CPADP (entries 1–2) and DDMAT (entries 3–5), respectively.[a)].

Entry	DP	$[OEOMA_{500}]_0$ (mM)	Time (hrs)	[b]Conv. (%)	$M_{n,the}$ x 1,000	[c]$M_{n,abs}$ x 1,000	[c]$Đ$
1	200	300	15.5	60	60.3	76.9	1.58
2	100	800	6	54	27.3	33.2	1.24
3	200	300	17	94	94.4	96.6	1.52
4[d]	200	300	2.1	55	55.4	58.8	1.41
5	50	600	4.5	81	20.7	21.6	1.20

(a) PET RAFT polymerization (entries 1–2) was carried out using CPADP as chain transfer agent with conditions: $[OEOMA_{500}]_0/[CPADP]_0/[EY]_0/[Et_3N]_0$ = 100–200/1/0.02/1 in H_2O and DMSO (10 % v/v). Photoiniferter RAFT polymerization (entries 3–5) was carried out using DDMAT as chain transfer agent with conditions: $[OEOMA_{500}]_0/[DDMAT]_0$ = 50–200/1 in DMSO, irradiated with iPhone 6 flashlights in a closed cap vial (1.5 mL). (b) Monomer conversion was determined by using ^1H NMR spectroscopy. (c) Molecular weight ($M_{n,\,abs}$) and dispersity ($Đ$) were determined by GPC analysis (DMF as eluent). Absolute molecular weight ($M_{n,\,abs}$) was determined using dn/dc values of $POEOMA_{500}$ = 0.05. Dispersity ($Đ$) values were recorded from refractive index GPC traces. (d) EvoluChem light (λ_{max} = 527 nm, 66.0 mW/cm^2) was used.

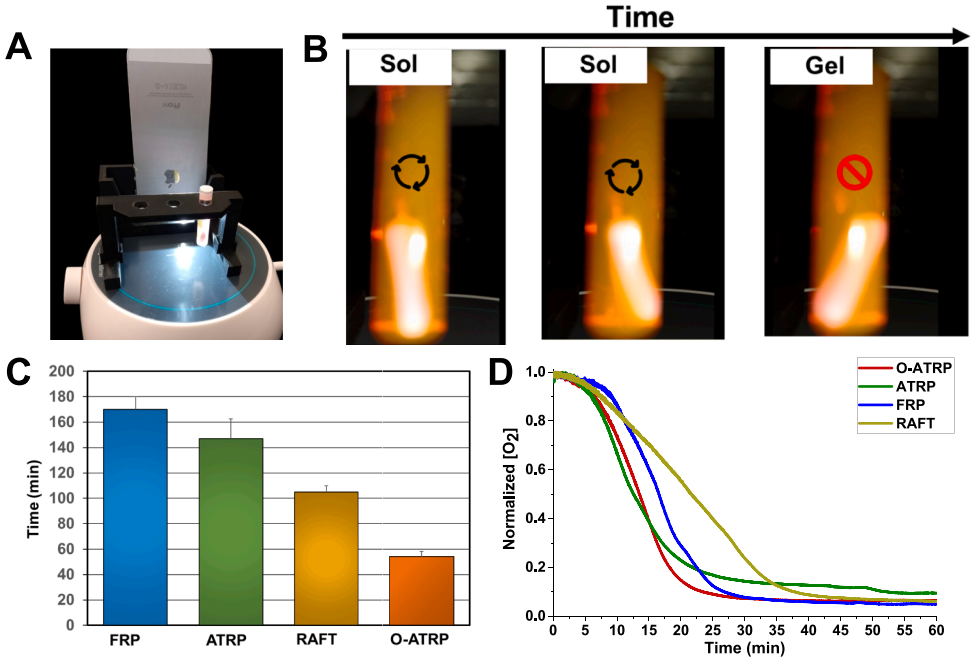


Fig. 3. (A) The set-up for the gelation experiment of $OEOMA_{500}$ in the presence of $DiOEOMA_{750}$. (B) Digital images of the gelation experiment captured by a smartphone camera while irradiating with smartphone flashlight. (C) Comparison of gelation point measurements and (D) oxygen reduction measurement profile under four different polymerization conditions.

[75,76]. Smartphone flashlight enabled activation of 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (DDMAT) without any additional additive and deoxygenation procedure (Scheme 2). Nevertheless, the polymerization was slow (17 h) and poorly controlled ($Đ$ = 1.52, entry 3, Table 2). The experiment with a commercial green light reactor (EvoluChem, λ_{max} = 527 nm, 66 mW/cm^2) generated polymers with only some improvement ($Đ$ = 1.41, entry 4, Table 2), suggesting that the limited control arises from the polymerization conditions rather than the inefficiency of the light source. Analogous to PET-RAFT, reducing target DP (DP = 50) while increasing $[OEOMA]_{500}$ = 600 mM afforded polymers with lower dispersity ($Đ$ = 1.20, entry 5, Table 2), generating one of the easiest and the most robust methods for synthesizing controlled polymers.

Oxyegn-tolerant gel formation. To further demonstrate the advantage of the smartphones as versatile synthetic tools and to display other enabling features of smartphones in polymer science, we used them for the efficient formation of crosslinked gels by copolymerization of $OEOMA_{500}$ and poly(ethylene glycol) dimethacrylate ($DiOEOMA_{750}$), and facile measurement of gel points by an in-built smartphone camera (Fig. 3A-B). The formation of crosslinked gels is typically used as a visual indication of analytes presence in radical polymerization reactions for amplified biodetection signals [47,77]. The formation of $OEOMA_{500}$ crosslinked gels was monitored by a smartphone camera via tracking stir bar rotation under four different polymerization conditions: (1) Free radical polymerization (FRP) with EY and TPMA (electron donor). (2) Organic ATRP (O-ATRP) with EY, TPMA and HOBiB. (3) ATRP with EY, TPMA, HOBiB and $CuBr_2$. (4) RAFT with EY, TPMA, and CPDAP. All experiments were carried out in triplicate and the results are shown in Fig. 3C. While the oxygen removal profile was relatively analogous under all polymerization conditions (Fig. 3D), the fastest gelation was observed in the order of O-ATRP > RAFT > ATRP > FRP. The most rapid gelation was observed in O-ATRP, suggesting the formation of high concentrations of radicals via activation of the HOBiB initiator by EY. The gelation process in ATRP and RAFT was slow due to the deactivation events induced by $CuBr_2$ and CPDAP which reduces the concentrations of radicals. When higher concentration of $CuBr_2$ or CPDAP was used, the formation of crosslinked gels was inhibited in 5 hr monitoring of the process. Overall, smartphone flashlights enabled the rapid and reproducible formation of crosslinked gels without rigorous deoxygenation procedure under all four polymerization conditions.

3. Conclusion

In conclusion, we demonstrated that visible light RDRP can be carried out with smartphones flashlight and conveniently provides well-controlled polymers employing commercially available reagents. Importantly, oxygen tolerance was conferred through the addition of photocatalytic dyes to the polymerization mixture (for both ATRP and PET-RAFT) or by the inherent oxygen scavenging ability of the system (for PI RAFT). Thus, this technique is very suitable for non-experts and in resource-limited settings. We envisage that smartphone provides easy and affordable access to a plethora of organic transformations and could enable RDRP to be widely applied outside of the synthetic chemistry laboratory, particularly for some emerging RDRP applications such as 3D printing [41], signal amplification [48], ultra-low scale polymerization [78], online reaction monitoring [79], as well as chemical education [80,81].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2023.112631.

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